CLAIMS

We claim:

- 5 1. A strength improvement admixture composition comprising:
 - a. polycarboxylate dispersant;
 - b. set retarder; and
 - c. a strength improvement additive selected from the group consisting of poly(hydroxyalkylated)polyethyleneamines,
- poly(hydroxyalkylated)polyethylenepolyamines,
 poly(hydroxyalkylated)polyethyleneimines,
 poly(hydroxyalkylated)polyamines, hydrazines, 1,2-diaminopropane,
 polyglycoldiamine, poly(hydroxyalkyl)amines and mixtures thereof.
- The admixture composition of claim 1, wherein the amount of polycarboxylate dispersant is from about 5% to about 80%, the set retarder is from about 0.5% to about 40%, and the strength improvement additive is from about 0.5% to about 40% based on the total dry weight of the admixture composition components.

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- 3. The admixture composition of claim 1, wherein the amount of polycarboxylate dispersant is from about 20% to about 60%, the set retarder is from about 2% to about 25%, and the strength improvement additive is from about 2% to about 25% based on the total dry weight of the admixture composition components.
- 4. The admixture composition of claim 1, wherein the strength improvement additive is selected from the group consisting of di(hydroxyethyl)1,2-diaminopropane, tetra(hydroxyethyl)1,2-diaminopropane, di(hydroxyethyl)hydrazine, tetra(hydroxyethyl)hydrazine, ethoxylated polyglycoldiamine, triisopropanolamine and mixtures thereof.

- 5. The admixture composition of claim 1, wherein the strength improvement group consisting additive is from of N,N,N'-triselected the N,N,N'-tri-(hydroxyethyl)diethylenediamine, (hydroxyethyl)ethylenediamine, N, N'-bis(2-N,N'-di-(hydroxyethyl)ethylenediamine, N.N.N',N'-5 hydroxypropyl)diethylenetriamine, tetra(hydroxyethyl)ethylenediamine, N,N,N',N',N"penta(hydroxyethyl)diethylenetriamine, N,N'-bis(2-hydroxypropyl)-N,N,N'tri(hydroxyethyl)diethylenetriamine, and mixtures thereof.
- 10 6. The admixture composition of claim 1, wherein the strength improvement additive comprises poly(hydroxyethyl)polyethyleneimine.
 - 7. The admixture composition of claim 1, wherein the strength improvement additive comprises poly(hydroxyalkylated)polyethyleneamine having the following formula:

$$(R)_2N[CH_2CH_2N]_xR \ | \ R$$

- wherein x is 1,2 or 3 and R is selected from the group consisting of hydrogen, 2-hydroxyethyl, and 2-hydroxypropyl, each R can be the same or different, and at least 40% of the R groups are hydroxyalkyl, with no more than 40% of the R groups being hydroxypropyl.
- 25 8. The admixture composition of claim 1, wherein the strength improvement additive has the following formula:

$$(R')_2NCH_2CH_2N(R')_2$$

- wherein R' is (CH₂CH₂O)_yH, wherein y is 0, 1 or 2, wherein no more than one-half (1/2) of the compounds of the formula have y equal to 0, and each R' can be the same or different.
 - 9. The admixture composition of claim 1, wherein the strength improvement additive has the following formula:

wherein R" is selected from the group consisting of (CH₂CH₂O)_yH and

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wherein X is a covalent bond or a divalent organic radical selected from the group consisting of CH₂, CH₂CH₂,

CH3 15 | CHCH2

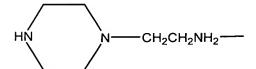
and CH2CH2CH2OCH2CH2OCH2CH2CH2CH2; wherein y and v are 0, 1

or 2;

wherein w is 0 or 1;

wherein v and w cannot both be 0; and wherein no more than one-half (1/2) of the R" groups are hydrogen.

10. The admixture composition of claim 1, wherein the strength improvement additive comprises Ethoxylated Amine HH, having a typical analysis of:



aminoethyl piperazine: triethylene tetramine:

50% to 70% by weight 40% maximum by weight

others:

balance.

11. The admixture composition of claim 1, wherein the strength improvement additive has the following formula:

 $(R^3)_nH_qN$

Wherein R^3 is $[(CHR^4)_m (CHR^4)O]_pH$;

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wherein R<sup>4</sup> is independently H or CH<sub>3</sub>;
wherein m = 1 or 2;
wherein n = 2 or 3;
wherein p = 1 or 2;
wherein q = 3-n
and each R<sup>3</sup> can be the same or different.
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12. The admixture composition of claim 1 wherein the set retarder is selected from the group consisting of an oxy-boron compound, a polyphosphonic acid, a carboxylic acid, a hydroxycarboxylic acid, polycarboxylic acid, hydroxylated carboxylic acid, fumaric, itaconic, malonic, borax, gluconic, and tartaric acid, lignosulfonates, ascorbic acid, isoascorbic acid, sulphonic acid-acrylic acid copolymer, and their corresponding salts, polyhydroxysilane, polyacrylamide, carbohydrates and mixtures thereof.

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- 13. The admixture composition of claim 1 further comprising at least one of set accelerators, air detraining agents, air entraining agents, shrinkage reducing admixtures, water reducers, foaming agents, dampproofing admixtures, pumping aids, fungicidal admixtures, insecticidal admixtures, germicidal admixtures, alkali activity reducers, bonding admixtures, corrosion inhibitors, and pigments.
- 14. The admixture composition of claim 1, wherein the admixture composition is in an aqueous solution.
- 15. A cementitious composition comprising hydraulic cement and a strength
 25 improvement admixture composition, said admixture composition comprising:
 - a. polycarboxylate dispersant;
 - b. set retarder; and
 - a strength improvement additive selected from the group consisting of a poly(hydroxyalkylated)polyethyleneamines,
- poly(hydroxyalkylated)polyethylenepolyamines, poly(hydroxyalkylated)polyethyleneimines,

poly(hydroxyalkylated)polyamines, hydrazines, 1,2-diaminopropane, polyglycoldiamine, poly(hydroxyalkyl)amines and mixtures thereof.

- 16. The cementitious composition of claim 15, wherein the amount of polycarboxylate dispersant is from about 0.02% to about 2%, the set retarder is from about 0.002% to about 0.2%, the strength improvement additive is from about 0.0001% to about 0.2% by weight of cementitious binder.
- 17. The cementitious composition of claim 15, wherein the amount of polycarboxylate dispersant is from about 0.02% to about 0.24%, the set retarder is from about 0.005% to about 0.08%, the strength improvement additive is from about 0.004% to about 0.08% by weight of cementitious binder.
- 15 18. The cementitious composition of claim 15, wherein the strength improvement additive is selected from the group consisting of di(hydroxyethyl)1,2-diaminopropane, tetra(hydroxyethyl)1,2-diaminopropane, di(hydroxyethyl)hydrazine, tetra(hydroxyethyl)hydrazine, ethoxylated polyglycoldiamine, triisopropanolamine and mixtures thereof.

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19. The cementitious composition of claim 15, wherein the strength improvement additive is selected from the group consisting of N,N,N'-tri-(hydroxyethyl)ethylenediamine, N,N,N'-tri-(hydroxyethyl)diethylenediamine, N,N'-di-(hydroxyethyl)ethylenediamine, N,N'-bis(2-

25 hydroxypropyl)diethylenetriamine, N,N,N',N'tetra(hydroxyethyl)ethylenediamine, N,N,N',N',N'penta(hydroxyethyl)diethylenetriamine, N,N'-bis(2-hydroxypropyl)-N,N,N'-

tri(hydroxyethyl)diethylenetriamine, and mixtures thereof.

30 20. The cementitious composition of claim 15, wherein the strength improvement additive comprises poly(hydroxyethyl)polyethyleneimine.

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21. The cementitious composition of claim 15, wherein the strength improvement additive comprises poly(hydroxyalkylated)polyethyleneamine having the following formula:

wherein x is 1,2 or 3 and R is selected from the group consisting of hydrogen, 2-hydroxyethyl, and 2-hydroxypropyl, each R can be the same or different, and at least 40% of the R groups are hydroxyalkyl, with no more than 40% of the R groups being hydroxypropyl.

22. The cementitious composition of claim 15, wherein the strength improvement additive has the following formula:

$$(R')_2NCH_2CH_2N(R')_2$$

wherein R' is (CH₂CH₂O)_yH, wherein y is 0, 1 or 2, wherein no more than one-half (1/2) of the compounds of the formula have y equal to 0, and each R' can be the same or different.

23. The cementitious composition of claim 15, wherein the strength improvement additive has the following formula:

$$(R")_2N[XN]_y[CH_2CH_2N]_wR"$$
 $|$
 $|$
 $R"$
 $R"$

CHCH₂

wherein R" is selected from the group consisting of (CH2CH2O)yH and

wherein X is a covalent bond or a divalent organic radical selected from the group consisting of CH₂, CH₂CH₂.

or 2;

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and CH₂CH₂CH₂OCH₂CH₂OCH₂CH₂CH₂CH₂; wherein y and v are 0, 1

wherein w is 0 or 1;

wherein v and w cannot both be 0; and wherein no more than one-half (1/2) of the R" groups are hydrogen.

24. The cementitious composition of claim 15, wherein the strength improvement additive comprises Ethoxylated Amine HH, having a typical analysis of:

HN N-CH₂CH₂NH₂-

aminoethyl piperazine: triethylene tetramine:

50% to 70% by weight 40% maximum by weight

others:

balance.

25. The admixture composition of claim 15, wherein the strength improvement additive has the following formula:

 $(R^3)_n H_q N$

Wherein R^3 is $[(CHR^4)_m (CHR^4)O]_pH$;

wherein R⁴ is independently H or CH₃;

wherein m = 1 or 2;

wherein n = 2 or 3;

wherein p = 1 or 2;

wherein q = 3-n;

and each R³ can be the same or different.

26. The cementitious composition of claim 15 wherein the set retarder is selected from the group consisting of an oxy-boron compound, a polyphosphonic acid, a carboxylic acid, a hydroxycarboxylic acid, polycarboxylic acid, hydroxylated carboxylic acid, fumaric, itaconic, malonic, borax, gluconic, and tartaric acid, lignosulfonates, ascorbic acid, isoascorbic acid, sulphonic acid-

acrylic acid copolymer, and their corresponding salts, polyhydroxysilane, polyacrylamide, carbohydrates and mixtures thereof.

- The cementitious composition of claim 15, wherein the cement is selected from the group consisting of portland cement, modified portland cement, or masonry cement, and mixtures thereof.
 - 28. The cementitious composition of claim 15 wherein the hydraulic cement is portland cement.
- The cementitious composition of claim 15 further comprising a cement 10 29. admixture or additive that is selected from the group consisting of set accelerator, air detraining agent, air entraining agent, foaming agent, corrosion inhibitor, shrinkage reducing admixture, water reducer, fiber, pigment, pozzolan, clay, strength enhancing agents, rheology modifying wetting agents, water soluble polymers, 15 agents, water repellents, dampproofing admixtures, gas formers, permeability reducers, pumping aids, fungicidal admixtures, germicidal admixtures, insecticidal admixtures, aggregates, alkali- reaction reducers, bonding admixtures, and mixtures thereof.
- 20 30. The cementitious composition of claim 29, wherein the aggregate is at least one of silica, quartz, crushed round marble, glass spheres, granite, limestone, calcite, feldspar, alluvial sands, and sand.
- The cementitious composition of claim 29, wherein the pozzolan is at least one of natural pozzolan, metakaolin, fly ash, silica fume, calcined clay, and blast furnace slag.
 - 32. The composition of claim 1 or 15 wherein the polycarboxylate dispersant comprises at least one of:
 - a) a dispersant of Formula (I):

wherein in Formula (I)

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- X is at least one of hydrogen, an alkali earth metal ion, an alkaline earth metal ion, ammonium ion, or amine;
- R is at least one of C₁ to C₆ alkyl(ene) ether or mixtures thereof or C₁ to C₆ alkyl(ene) imine or mixtures thereof;
 - Q is at least one of oxygen, NH, or sulfur;
 - p is a number from 1 to about 300 resulting in at least one of a linear side chain or branched side chain;
- 10 R₁ is at least one of hydrogen, C₁ to C₂₀ hydrocarbon, or functionalized hydrocarbon containing at least one of -OH, -COOH, an ester or amide derivative of -COOH, sulfonic acid, an ester or amide derivative of sulfonic acid, amine, or epoxy;
 - Y is at least one of hydrogen, an alkali earth metal ion, an alkaline earth metal ion, ammonium ion, amine, a hydrophobic hydrocarbon or polyalkylene oxide moiety that functions as a defoamer;
 - m, m', m'', n, n', and n'' are each independently 0 or an integer between 1 and about 20;
 - Z is a moiety containing at least one of i) at least one amine and one acid group, ii) two functional groups capable of incorporating into the backbone selected from the group consisting of dianhydrides, dialdehydes, and di-acid-chlorides, or iii) an imide residue; and

wherein a, b, c, and d reflect the mole fraction of each unit wherein the sum of a, b, c, and d equal one, wherein a, b, c, and d are each a value greater than or equal to zero and less than one, and at least two of a, b, c, and d are greater than zero;

b) a dispersant of Formula (II):

wherein in Formula (II):

A is COOM or optionally in the "y" structure an acid anhydride group (-CO-O-CO-) is formed in place of the A groups between the carbon atoms to which the A groups are bonded to form an anhydride;

B is COOM

M is hydrogen, a transition metal cation, the residue of a hydrophobic polyalkylene glycol or polysiloxane, an alkali metal ion, an alkaline earth metal ion, ferrous ion, aluminum ion, (alkanol)ammonium ion, or (alkyl)ammonium ion;

R is a C₂₋₆ alkylene radical;

R1 is a C₁₋₂₀ alkyl, C₆₋₉ cycloalkyl, or phenyl group;

x, y, and z are a number from 0.01 to 100;

m is a number from 1 to 100; and

n is a number from 10 to 100;

- c) a dispersant comprising at least one polymer or a salt thereof having the form of a copolymer of
 - i) a maleic anhydride half-ester with a compound of the formula RO(AO)_mH, wherein R is a C₁-C₂₀ alkyl group, A is a C₂₋₄ alkylene group, and m is an integer from 2-16; and
 - ii) a monomer having the formula CH₂=CHCH₂-(OA)_nOR, wherein n is an integer from 1-90 and R is a C₁₋₂₀ alkyl group;

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d) a dispersant obtained by copolymerizing 5 to 98% by weight of an (alkoxy)polyalkylene glycol mono(meth)acrylic ester monomer (a) represented by the following general formula (1):

$$\begin{array}{c}
R_5 \\
CH \longrightarrow C \longrightarrow R_1 \\
COO(R_2O)_{\underline{m}}R_3
\end{array}$$
(1)

$$\begin{array}{c}
R_5 \\
CH \longrightarrow C \longrightarrow R_4 \\
COOM_1
\end{array}$$
(2)

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wherein R₁ stands for hydrogen atom or a methyl group, R₂O for one species or a mixture of two or more species of oxyalkylene group of 2 to 4 carbon atoms, providing two or more species of the mixture may be added either in the form of a block or in a random form, R₃ for a hydrogen atom or an alkyl group of 1 to 5 carbon atoms, and m is a value indicating the average addition mol number of oxyalkylene groups that is an integer in the range of 1 to 100, 95 to 2% by weight of a (meth)acrylic acid monomer (b) represented by the above general formula (2), wherein R₄ and R₅ are each independently a hydrogen atom or a methyl group, and M₁ for a hydrogen atom, a monovalent metal atom, a divalent metal atom, an ammonium group, or an organic amine group, and 0 to 50% by weight of other monomer (c) copolymerizable with these monomers, provided that the total amount of (a), (b), and (c) is 100% by weight;

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- e) a graft polymer that is a polycarboxylic acid or a salt thereof, having side chains derived from at least one species selected from the group consisting of oligoalkyleneglycols, polyalcohols, polyoxyalkylene amines, and polyalkylene glycols;
- f) a dispersant of Formula (III):

$$\begin{array}{c|c} & & & \\ & & \\ \hline \\ CH_2 & C \\ CH_2 & C \\ \hline \\ CH_2 & C \\ CH_2 & C \\ \hline \\ CH_2 & C \\ CH_2 & C \\ \hline \\ CH_2 & C \\ CH_2 &$$

wherein in Formula (III):

D = a component selected from the group consisting of the structure d1, the structure d2, and mixtures thereof;

X = H, CH₃, C₂ to C₆ Alkyl, Phenyl, p-Methyl Phenyl, or Sulfonated Phenyl;

Y = H or -COOM;

 $R = H \text{ or } CH_3$;

 $Z = H_1 - SO_3M_1 - PO_3M_1 - COOM_1 - O(CH_2)_nOR_3$ where n = 2 to 6,

-COOR₃, or -(CH₂)_nOR₃ where n = 0 to 6,

-CONHR₃, -CONHC(CH₃)₂ CH₂SO₃M, -COO(CHR₄)_nOH where n=2 to 6, or -O(CH₂)_nOR₄ wherein n=2 to 6;

R₁, R₂, R₃, R₅ are each independently -(CHRCH₂O)_mR₄ random copolymer of oxyethylene units and oxypropylene units where m = 10 to 500 and wherein the amount of oxyethylene in the random copolymer is from about 60% to 100% and the amount of oxypropylene in the random copolymer is from 0% to about 40%;

 $R_4 = H$, Methyl, C_2 to about C_6 Alkyl, or about C_6 to about C_{10} aryl;

M = H, Alkali Metal, Alkaline Earth Metal, Ammonium, Amine, triethanol amine, Methyl, or C₂ to about C₆ Alkyl;

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a = 0 to about 0.8;

b = about 0.2 to about 1.0;

c = 0 to about 0.5;

d = 0 to about 0.5; and

wherein a, b, c, and d represent the mole fraction of each unit and the sum of a, b, c, and d is 1.0;

g) a dispersant of Formula (IV):

wherein in Formula (IV):

the "b" structure is one of a carboxylic acid monomer, an ethylenically unsaturated monomer, or maleic anhydride wherein an acid anhydride group (-CO-O-CO-) is formed in place of the groups Y and Z between the carbon atoms to which the groups Y and Z are bonded respectively, and the "b" structure must include at least one moiety with a pendant ester linkage and at least one moiety with a pendant amide linkage;

X = H, CH₃, C₂ to C₆ Alkyl, Phenyl, p-Methyl Phenyl, p-Ethyl Phenyl, Carboxylated Phenyl, or Sulfonated Phenyl;

Y = H, -COOM, -COOH, or W;

W = a hydrophobic defoamer represented by the formula R₅O-(CH₂CH₂O)_s-(CH₂C(CH₃)HO)_t-(CH₂CH₂O)_u where s, t, and u are integers from 0 to 200 with the proviso that t>(s+u) and wherein the total amount of hydrophobic defoamer is present in an amount less than about 10% by weight of the polycarboxylate dispersant;

Z = H, -COOM, -O(CH₂)_nOR₃ where n = 2 to 6, -COOR₃, -(CH₂)_nOR₃ where n = 0 to 6, or -CONHR₃;

 $R_1 = H$, or CH_3 ;

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R₂, R₃, are each independently a random copolymer of oxyethylene units and oxypropylene units of the general formula -(CH(R₁)CH₂O)_mR₄ where m=10 to 500 and wherein the amount of oxyethylene in the random copolymer is from about 60% to 100% and the amount of oxypropylene in the random copolymer is from 0% to about 40%;

 $R_4 = H$, Methyl, or C_2 to C_8 Alkyl;

 $R_5 = C_1$ to C_{18} alkyl or C_6 to C_{18} alkyl aryl;

M = Alkali Metal, Alkaline Earth Metal, Ammonia, Amine, monoethanol amine, diethanol amine, triethanol amine, morpholine, imidazole;

a = 0.01-0.8;

b = 0.2-0.99;

c = 0-0.5; and

wherein a, b, c represent the mole fraction of each unit and the sum of a, b, and c, is 1;

h) a random copolymer corresponding to the following Formula (V) in free acid or salt form having the following monomer units and numbers of monomer units:

wherein A is selected from the moieties (i) or (ii)

(i)
$$-CR_1R_2-CR_3R_4$$
 (ii)

wherein R₁ and R₃ are selected from substituted benzene, C₁₋₈ alkyl, C₂₋₈ alkenyl, C₂₋₈ alkylcarbonyl, C₁₋₈ alkoxy, carboxyl, hydrogen, and a

ring, R2 and R4 are selected from the group consisting of hydrogen and C₁₋₄ alkyl, wherein R₁ and R₃ can together with R₂ and/or R₄ when R₂ and/or R₄ are C₁₋₄ alkyl form the ring; R₇, R₈, R₉, and R₁₀ are individually selected from the group consisting of hydrogen, C₁₋₆ alkyl, and a C₂₋₈ hydrocarbon chain, wherein R₁ and 5 R₃ together with R₇ and/or R₈, R₉, and R₁₀ form the C₂₋₈ hydrocarbon chain joining the carbon atoms to which they are attached, the hydrocarbon chain optionally having at least one anionic group, wherein the at least one anionic group is optionally sulfonic; 10 M is selected from the group consisting of hydrogen, and the residue of a hydrophobic polyalkylene glycol or a polysiloxane, with the proviso that when A is (ii) and M is the residue of a hydrophobic polyalkylene glycol, M must be different from the group -(R₅O)_mR₆; R₅ is a C₂₋₈ alkylene radical; R₆ is selected from the group consisting of C₁₋₂₀ alkyl, C₆₋₉ cycloalkyl 15 and phenyl; n, x, and z are numbers from 1 to 100; y is 0 to 100; m is 2 to 1000; 20 the ratio of x to (y+z) is from 1:10 to 10:1 and the ratio of y:z is from 5:1 to 1:100; a copolymer of oxyalkyleneglycol-alkenyl ethers and unsaturated i) dicarboxylic acids, comprising: i) 0 to 90 mol % of at least one component of the formula 3a or 25 3b:

wherein M is a hydrogen atom, a mono- or divalent metal cation, an ammonium ion or an organic amine residue, a is 1, or when M is a divalent metal cation a is $\frac{1}{2}$;

wherein X is -OM_a,

-O-(C_mH_{2m}O)_n-R¹ in which R¹ is a hydrogen atom, an aliphatic hydrocarbon radical containing from 1 to 20 carbon atoms, a cycloaliphatic hydrocarbon radical containing 5 to 8 carbon atoms or an optionally hydroxyl, carboxyl, C₁₋₁₄ alkyl, or sulphonic substituted aryl radical containing 6 to 14 carbon atoms, m is 2 to 4, and n is 0 to 100,

-NHR₂,-N(R²)₂ or mixtures thereof in which $R^2=R^1$ or -CO-NH₂; and

wherein Y is an oxygen atom or -NR²;

ii) 1 to 89 mol% of components of the general formula 4:

$$---CH_2$$
 $---CR^3$ (4)
 $(CH_2)_p$ $----C(C_mH_{2m}O)_n$ $----R^1$

wherein R₃ is a hydrogen atom or an aliphatic hydrocarbon radical containing from 1 to 5 carbon atoms, p is 0 to 3, and R₁ is hydrogen, an aliphatic hydrocarbon radical containing from 1 to 20 carbon atoms, a cycloaliphatic hydrocarbon radical containing 5 to 8 carbon atoms or an optionally hydroxyl, carboxyl, C₁₋₁₄ alkyl, or sulfonic substituted

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aryl radical containing 6 to 14 carbon atoms, m is 2 to 4, and n is 0 to 100, and

iii) 0.1 to 10 mol % of at least one component of the formula 5a or 5b:

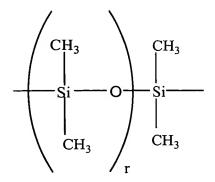
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wherein S is a hydrogen atom or -COOM_a or -COOR₅, T is -COOR₅, -W-R₇, -CO-[-NH-(CH2)3)-]_s-W-R₇, -CO-O-(CH₂)_z-W-R₇, a radical of the general formula:

$$\frac{---U^{1} \left(CH - CH_{2} - O \right)_{x} \left(CH_{2} - CH_{2} - O \right)_{y} R^{6}}{CH_{3}}$$

or $-(CH_2)_z$ -V- $(CH_2)_z$ -CH=CH-R₁, or when S is $-COOR_5$ or $-COOM_a$, U₁ is -CO-NHM-, -O- or $-CH_2O$, U₂ is -NH-CO-, -O- or $-OCH_2$, V
is -O-CO-C₆H₄-CO-O- or -W-, and W is



R4 is a hydrogen atom or a methyl radical, R5 is an aliphatic hydrocarbon radical containing 3 to 20 carbon atoms, a cycloaliphatic hydrocarbon radical containing 5 to 8 carbon atoms or an aryl radical containing 6 to 14 carbon atoms, $R_6=R_1$ or

 $---CH_2---CH---U^2-C=-CH$ $\downarrow \qquad \qquad \downarrow \qquad \qquad \downarrow$ $R^4 \qquad \qquad R^4 \qquad S$

 $R_7 = R_1$ or

 $--\left\{ \left(CH_{2}\right) _{3}--NH\right\} -CO-CH$ $R^{4}-S$

or

--- (CH₂)_Z --- O----CO -- C=-CH----- $\begin{vmatrix} & & & \\ &$

r is 2 to 100, s is 1 or 2, x is 1 to 150, y is 0 to 15 and z is 0 to 4;

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0 to 90 mol % of at least one component of the formula 6a, 6b, iv) or 6c:

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wherein M is a hydrogen atom, a mono- or divalent metal cation, an ammonium ion or an organic amine residue, a is 1, or when M is a divalent metal cation a is ½;

wherein X is -OMa,

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-O-(C_mH_{2m}O)_n-R¹ in which R¹ is a hydrogen atom, an aliphatic hydrocarbon radical containing from 1 to 20 carbon atoms, a cycloaliphatic hydrocarbon radical containing 5 to 8 carbon atoms or an optionally hydroxyl, carboxyl, C₁₋₁₄ alkyl, or sulphonic substituted aryl radical containing 6 to 14 carbon atoms, m is 2 to 4, and n is 0 to 100,

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- $-NH-(C_mH_{2m}O)_n-R^1$,
- $-NHR_2, -N(R^2)_2$ or mixtures thereof in which $R^2 = R^1$ or
- -CO-NH₂; and

wherein Y is an oxygen atom or -NR²;

- a copolymer of dicarboxylic acid derivatives and oxyalkylene glycolj) alkenyl ethers, comprising:
 - i) 1 to 90 mol. % of at least one member selected from the group consisting of structural units of formula 7a and formula 7b:

$$\begin{array}{c|c} \hline CH \hline CH \hline \\ \hline \\ COOM_a & COR^1 \\ \hline \end{array}$$
 (7a)

wherein M is H, a monovalent metal cation, a divalent metal cation, an ammonium ion or an organic amine;

a is ½ when M is a divalent metal cation or 1 when M is a monovalent metal cation;

wherein R1 is -OMa, or

 $-O-(C_mH_{2m}O)_n-R^2$ wherein R^2 is H, a C_{1-20} aliphatic hydrocarbon, a C_{5-8} cycloaliphatic hydrocarbon, or a C_{6-14} aryl that is optionally substituted with at least one member selected from the group consisting of $-COOM_a$, $-(SO_3)M_a$, and $-(PO_3)M_{a2}$;

m is 2 to 4; n is 1 to 200;

ii) 0.5 to 80 mol. % of the structural units of formula 8:

wherein R³ is H or a C1-5 aliphatic hydrocarbon;

p is 0 to 3;

 R^2 is H, a C_{1-20} aliphatic hydrocarbon, a C_{5-8} cycloaliphatic hydrocarbon, or a C_{6-14} aryl that is optionally substituted with at least one member selected from the group consisting of $-COOM_a$, $-(SO_3)M_a$, and $-(PO_3)$ M_{a2} ;

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m is 2 to 4; n is 1 to 200;

iii) 0.5 to 80 mol.% structural units selected from the group consisting of formula 9a and formula 9b:

wherein R^4 is H, C_{1-20} aliphatic hydrocarbon that is optionally substituted with at least one hydroxyl group, $-(C_mH_{2m}O)_n-R^2$, —

CO-NH-R², C₅₋₈ cycloaliphatic hydrocarbon, or a C₆₋₁₄ aryl that is optionally substituted with at least one member selected from the group consisting of -COOM_a, -(SO₃)M_a, and -(PO₃)M_{a2};

M is H, a monovalent metal cation, a divalent metal cation, an ammonium ion or an organic amine;

a is ½ when M is a divalent metal cation or 1 when M is a monovalent metal cation;

 R^2 is H, a C_{1-20} aliphatic hydrocarbon, a C_{5-8} cycloaliphatic hydrocarbon, or a C_{6-14} aryl that is optionally substituted with at least one member selected from the group consisting of $-COOM_a$, $-(SO_2)M_{-2}$ and $-(PO_2)M_{-2}$:

(SO₃)M_a, and -(PO₃)M_{a2};

m is 2 to 4; n is 1 to 200;

iv) 1 to 90 mol. % of structural units of formula 10

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$$\begin{array}{c|c}
R^6 \\
\hline
\\
CH - C - \\
\downarrow \\
R^5 R^7
\end{array} (10)$$

wherein R⁵ is methyl, or methylene group, wherein R⁵ forms one or more 5 to 8 membered rings with R⁷;

R⁶ is H, methyl, or ethyl;

R⁷ is H, a C₁₋₂₀ aliphatic hydrocarbon, a C₆₋₁₄ aryl that is optionally substituted with at least one member selected from the group consisting of -COOM_a, -(SO₃)M_a, and -(PO₃)M_a², a C₅₋₈ cycloaliphatic hydrocarbon, -OCOR⁴, -OR⁴, and -COOR⁴, wherein R⁴ is H, a C₁₋₂₀ aliphatic hydrocarbon that is optionally substituted with at least one -OH, -(C_mH_{2m}O)_n-R², -CO-NH-R², C₅₋₈ cycloaliphatic hydrocarbon, or a C₆₋₁₄ aryl residue that is optionally substituted with a member selected from the group consisting of -COOM_a, -(SO₃)M_a, and -(PO₃)M_{a2}.

- 33. A method of making a cementitious composition comprising forming a mixture of water, hydraulic cement and a strength improvement admixture composition, said admixture composition comprising the components of:
 - a. polycarboxylate dispersant;
 - b. set retarder; and
 - c. a strength improvement additive selected from the group consisting of poly(hydroxyalkylated)polyethyleneamines, poly(hydroxyalkylated)polyethylenepolyamines, poly(hydroxyalkylated)polyethyleneimines, poly(hydroxyalkylated)polyamines, hydrazines, 1,2-diaminopropane, polyglycoldiamine, poly(hydroxyalkyl)amines and mixtures thereof.

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34. The method of claim 33, wherein the amount of polycarboxylate dispersant is from about 0.02% to about 2%, the set retarder is from about 0.002% to about 0.2%, the strength improvement additive is from about 0.0001% to about 0.2% by weight of cementitious binder.

35. The method of claim 33, wherein the amount of polycarboxylate dispersant is from about 0.02% to about 0.24%, the set retarder is from about 0.005% to about 0.08%, the strength improvement additive is from about 0.004% to about 0.08% by weight of cementitious binder.

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- 36. The method of claim 33, wherein the strength improvement additive is selected from the group consisting of di(hydroxyethyl)1,2-diaminopropane, tetra(hydroxyethyl)1,2-diaminopropane, di(hydroxyethyl)hydrazine, tetra(hydroxyethyl)hydrazine, ethoxylated polyglycoldiamine, triisopropanolamine and mixtures thereof.
- The method of claim 33, wherein the strength improvement additive is selected from the group consisting of N,N,N'-tri-(hydroxyethyl)ethylenediamine, N,N,N'-tri-(hydroxyethyl)diethylenediamine, N,N'-di(hydroxyethyl)ethylenediamine, N,N'-bis(2-hydroxypropyl)diethylenetriamine, N,N,N',N'-tetra(hydroxyethyl)ethylenediamine, N,N'-bis(2-hydroxypropyl)-N,N,N'-penta(hydroxyethyl)diethylenetriamine, N,N'-bis(2-hydroxypropyl)-N,N,N'-tri(hydroxyethyl)diethylenetriamine, and mixtures thereof.
- 20 38. The method of claim 33, wherein the strength improvement additive comprises poly(hydroxyethyl)polyethyleneimine.
 - 39. The method of claim 33, wherein the strength improvement additive comprises poly(hydroxyalkylated)polyethyleneamine having the following formula:

(R)2N[CH2CH2N]xR | R

wherein x is 1,2 or 3 and R is selected from the group consisting of hydrogen,

2-hydroxyethyl, and 2-hydroxypropyl, each R can be the same or different, and
at least 40% of the R groups are hydroxyalkyl, with no more than 40% of the
R groups being hydroxypropyl.

40. The method of claim 33, wherein the strength improvement additive has the following formula:

 $(R')_2NCH_2CH_2N(R')_2$

- wherein R' is (CH₂CH₂O)_yH, wherein y is 0, 1 or 2, wherein no more than one-half (1/2) of the compounds of the formula have y equal to 0, and each R' can be the same or different.
- 41. The method of claim 33, wherein the strength improvement additive has the following formula:

wherein R" is selected from the group consisting of (CH₂CH₂O)_yH and

CH3

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wherein X is a covalent bond or a divalent organic radical selected from the group consisting of CH₂, CH₂CH₂,

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| CHCH2

- and CH₂CH₂OCH₂CH₂OCH₂CH₂OCH₂CH₂CH₂; wherein y and v are 0, 1 or 2;
- wherein w is 0 or 1; wherein v and w cannot both be 0; and wherein no more than one-half (1/2) of the R" groups are hydrogen.
- The method of claim 33, wherein the strength improvement additive comprisesEthoxylated Amine HH, having a typical analysis of:

aminoethyl piperazine: triethylene tetramine:

50% to 70% by weight 40% maximum by weight

others:

balance.

43. The admixture composition of claim 33, wherein the strength improvement additive has the following formula:

 $(R^3)_nH_qN$

5 Wherein R^3 is $[(CHR^4)_m (CHR^4)O]_pH$;

wherein R⁴ is independently H or CH₃;

wherein m = 1 or 2;

wherein n = 2 or 3;

wherein p = 1 or 2;

wherein q = 3-n;

and each R³ can be the same or different.

44. The method of claim 33 wherein the set retarder is selected from the group consisting of an oxy-boron compound, a polyphosphonic acid, a carboxylic acid, a hydroxycarboxylic acid, polycarboxylic acid, hydroxylated carboxylic acid, fumaric, itaconic, malonic, borax, gluconic, and tartaric acid, lignosulfonates, ascorbic acid, isoascorbic acid, sulphonic acid-acrylic acid copolymer, and their corresponding salts, polyhydroxysilane, polyacrylamide, carbohydrates and mixtures thereof.

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- 45. The method of claim 33, wherein the cement is selected from the group consisting of portland cement, modified portland cement, or masonry cement, and mixtures thereof.
- 46. The method of claim 33 wherein the hydraulic cement is portland cement.

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47. The method of claim 33 further comprising a cement admixture or additive that is selected from the group consisting of set accelerator, air detraining

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agent, air entraining agent, foaming agent, corrosion inhibitor, shrinkage reducing admixture, water reducer, fiber, pigment, pozzolan, clay, strength enhancing agents, rheology modifying agents, water repellents, wetting agents, water soluble polymers, dampproofing admixtures, gas formers, permeability reducers, pumping aids, fungicidal admixtures, germicidal admixtures, insecticidal admixtures, aggregates, alkali- reaction reducers, bonding admixtures, and mixtures thereof.

- 48. The method of claim 47, wherein the aggregate is at least one of silica, quartz, crushed round marble, glass spheres, granite, limestone, calcite, feldspar, alluvial sands, and sand.
- 49. The method of claim 47, wherein the pozzolan is at least one of natural pozzolan, metakaolin, fly ash, silica fume, calcined clay, and blast furnace slag.
- 15 50. The method of claim 33 wherein the polycarboxylate dispersant comprises at least one of:
 - a) a dispersant of Formula (I):

wherein in Formula (I)

20 X is at least one of hydrogen, an alkali earth metal ion, an alkaline earth metal ion, ammonium ion, or amine;

R is at least one of C₁ to C₆ alkyl(ene) ether or mixtures thereof or C₁ to C₆ alkyl(ene) imine or mixtures thereof;

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Q is at least one of oxygen, NH, or sulfur;

p is a number from 1 to about 300 resulting in at least one of a linear side chain or branched side chain;

R₁ is at least one of hydrogen, C₁ to C₂₀ hydrocarbon, or functionalized hydrocarbon containing at least one of -OH, -COOH, an ester or amide derivative of -COOH, sulfonic acid, an ester or amide derivative of sulfonic acid, amine, or epoxy;

Y is at least one of hydrogen, an alkali earth metal ion, an alkaline earth metal ion, ammonium ion, amine, a hydrophobic hydrocarbon or polyalkylene oxide moiety that functions as a defoamer;

m, m', m'', n, n', and n'' are each independently 0 or an integer between 1 and about 20;

Z is a moiety containing at least one of i) at least one amine and one acid group, ii) two functional groups capable of incorporating into the backbone selected from the group consisting of dianhydrides, dialdehydes, and di-acid-chlorides, or iii) an imide residue; and

wherein a, b, c, and d reflect the mole fraction of each unit wherein the sum of a, b, c, and d equal one, wherein a, b, c, and d are each a value greater than or equal to zero and less than one, and at least two of a, b, c, and d are greater than zero;

b) a dispersant of Formula (II):

wherein in Formula (II):

A is COOM or optionally in the "y" structure an acid anhydride group (-CO-O-CO-) is formed in place of the A groups between the carbon atoms to which the A groups are bonded to form an anhydride;

B is COOM

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M is hydrogen, a transition metal cation, the residue of a hydrophobic polyalkylene glycol or polysiloxane, an alkali metal ion, an alkaline earth metal ion, ferrous ion, aluminum ion, (alkanol)ammonium ion, or (alkyl)ammonium ion;

R is a C₂₋₆ alkylene radical;

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R1 is a C₁₋₂₀ alkyl, C₆₋₉ cycloalkyl, or phenyl group;

x, y, and z are a number from 0.01 to 100;

m is a number from 1 to 100; and

n is a number from 10 to 100;

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- c) a dispersant comprising at least one polymer or a salt thereof having the form of a copolymer of
 - i) a maleic anhydride half-ester with a compound of the formula RO(AO)_mH, wherein R is a C₁-C₂₀ alkyl group, A is a C₂₋₄ alkylene group, and m is an integer from 2-16; and

- ii) a monomer having the formula $CH_2 = CHCH_2 (OA)_nOR$, wherein n is an integer from 1-90 and R is a C_{1-20} alkyl group;
- a dispersant obtained by copolymerizing 5 to 98% by weight of an (alkoxy)polyalkylene glycol mono(meth)acrylic ester monomer (a) represented by the following general formula (1):

$$\begin{array}{c}
R_5 \\
CH \longrightarrow C \longrightarrow R_1 \\
COO(R_2O)_{\underline{m}}R_3
\end{array} (1)$$

$$\begin{array}{c}
\mathsf{R}_{5} \\
\mathsf{CH} \longrightarrow \mathsf{C} \longrightarrow \mathsf{R}_{4} \\
\mathsf{COOM}_{1}
\end{array}$$
(2)

wherein R₁ stands for hydrogen atom or a methyl group, R₂O for one species or a mixture of two or more species of oxyalkylene group of 2 to 4 carbon atoms, providing two or more species of the mixture may be added either in the form of a block or in a random form, R₃ for a hydrogen atom or an alkyl group of 1 to 5 carbon atoms, and m is a value indicating the average addition mol number of oxyalkylene groups that is an integer in the range of 1 to 100, 95 to 2% by weight of a (meth)acrylic acid monomer (b) represented by the above general formula (2), wherein R₄ and R₅ are each independently a hydrogen atom or a methyl group, and M₁ for a hydrogen atom, a monovalent metal atom, a divalent metal atom, an ammonium group, or an organic amine group, and 0 to 50% by weight of other monomer (c) copolymerizable with these monomers, provided that the total amount of (a), (b), and (c) is 100% by weight;

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- e) a graft polymer that is a polycarboxylic acid or a salt thereof, having side chains derived from at least one species selected from the group consisting of oligoalkyleneglycols, polyalcohols, polyoxyalkylene amines, and polyalkylene glycols;
- 20 f) a dispersant of Formula (III):

$$\begin{array}{c|c}
-\left(CH_2 - CH_2 - CH_$$

$$\begin{array}{c|c}
 & CH_2 & C & CH_2 & C \\
\hline
 & CH_2 & C & CH_2 \\
\hline
 & CH_2 & C & CH_2 \\
\hline
 & CH_2 & C & CH_2 \\
\hline
 & R & R \\
\hline
 & CH_2 & C & CH_2 \\
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 & R & C & C & CH_2 \\
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 & R & C & C & C & CH_2 \\
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 & R & C & C & C & C & C \\
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 & R & C & C & C & C & C \\
\hline
 & R & C & C & C & C &$$

wherein in Formula (III):

D = a component selected from the group consisting of the structure d1, the structure d2, and mixtures thereof;

X = H, CH₃, C₂ to C₆ Alkyl, Phenyl, p-Methyl Phenyl, or Sulfonated Phenyl;

Y = H or -COOM;

 $R = H \text{ or } CH_3;$

 $Z = H, -SO_3M, -PO_3M, -COOM, -O(CH_2)_nOR_3 \text{ where } n=2 \text{ to } 6,$ $-COOR_3, \text{ or } -(CH_2)_nOR_3 \text{ where } n=0 \text{ to } 6,$ $-CONHR_3, -CONHC(CH_3)_2 \text{ CH}_2SO_3M, -COO(CHR_4)_nOH \text{ where } n=2 \text{ to } 6, \text{ or } -O(CH_2)_nOR_4 \text{ wherein } n=2 \text{ to } 6;$

R₁, R₂, R₃, R₅ are each independently –(CHRCH₂O)_mR₄ random copolymer of oxyethylene units and oxypropylene units where m = 10 to 500 and wherein the amount of oxyethylene in the random copolymer is from about 60% to 100% and the amount of oxypropylene in the random copolymer is from 0% to about 40%;

 $R_4 = H$, Methyl, C_2 to about C_6 Alkyl, or about C_6 to about C_{10} aryl;

M = H, Alkali Metal, Alkaline Earth Metal, Ammonium, Amine, triethanol amine, Methyl, or C₂ to about C₆ Alkyl;

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a = 0 to about 0.8;

b = about 0.2 to about 1.0;

c = 0 to about 0.5;

d = 0 to about 0.5; and

wherein a, b, c, and d represent the mole fraction of each unit and the sum of a, b, c, and d is 1.0;

g) a dispersant of Formula (IV):

wherein in Formula (IV):

the "b" structure is one of a carboxylic acid monomer, an ethylenically unsaturated monomer, or maleic anhydride wherein an acid anhydride group (-CO-O-CO-) is formed in place of the groups Y and Z between the carbon atoms to which the groups Y and Z are bonded respectively, and the "b" structure must include at least one moiety with a pendant ester linkage and at least one moiety with a pendant amide linkage;

X = H, CH₃, C₂ to C₆ Alkyl, Phenyl, p-Methyl Phenyl, p-Ethyl Phenyl, Carboxylated Phenyl, or Sulfonated Phenyl;

Y = H, -COOM, -COOH, or W;

W = a hydrophobic defoamer represented by the formula R₅O-(CH₂CH₂O)_s-(CH₂C(CH₃)HO)_t-(CH₂CH₂O)_u where s, t, and u are integers from 0 to 200 with the proviso that t>(s+u) and wherein the total amount of hydrophobic defoamer is present in an amount less than about 10% by weight of the polycarboxylate dispersant;

 $Z = H, -COOM, -O(CH_2)_nOR_3 \mbox{ where } n=2 \mbox{ to } 6, -COOR_3, -(CH_2)_nOR_3 \mbox{ }$ where n=0 to 6, or $-CONHR_3;$

 $R_1 = H$, or CH_3 ;

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R₂, R₃, are each independently a random copolymer of oxyethylene units and oxypropylene units of the general formula $-(CH(R_1)CH_2O)_mR_4$ where m=10 to 500 and wherein the amount of oxyethylene in the random copolymer is from about 60% to 100% and the amount of oxypropylene in the random copolymer is from 0% to about 40%;

 $R_4 = H$, Methyl, or C_2 to C_8 Alkyl;

 $R_5 = C_1$ to C_{18} alkyl or C_6 to C_{18} alkyl aryl;

M = Alkali Metal, Alkaline Earth Metal, Ammonia, Amine, monoethanol amine, diethanol amine, triethanol amine, morpholine, imidazole;

a = 0.01-0.8;

b = 0.2-0.99;

c = 0-0.5; and

wherein a, b, c represent the mole fraction of each unit and the sum of a, b, and c, is 1;

h) a random copolymer corresponding to the following Formula (V) in free acid or salt form having the following monomer units and numbers of monomer units:

wherein A is selected from the moieties (i) or (ii)

wherein R₁ and R₃ are selected from substituted benzene, C₁₋₈ alkyl, C₂₋₈ alkenyl, C₂₋₈ alkylcarbonyl, C₁₋₈ alkoxy, carboxyl, hydrogen, and a

ring, R₂ and R₄ are selected from the group consisting of hydrogen and C₁₋₄ alkyl, wherein R₁ and R₃ can together with R₂ and/or R₄ when R₂ and/or R₄ are C₁₋₄ alkyl form the ring; R₇, R₈, R₉, and R₁₀ are individually selected from the group consisting of hydrogen, C₁₋₆ alkyl, and a C₂₋₈ hydrocarbon chain, wherein R₁ and 5 R₃ together with R₇ and/or R₈, R₉, and R₁₀ form the C₂₋₈ hydrocarbon chain joining the carbon atoms to which they are attached, the hydrocarbon chain optionally having at least one anionic group, wherein the at least one anionic group is optionally sulfonic; 10 M is selected from the group consisting of hydrogen, and the residue of a hydrophobic polyalkylene glycol or a polysiloxane, with the proviso that when A is (ii) and M is the residue of a hydrophobic polyalkylene glycol, M must be different from the group -(RsO)mR6; R₅ is a C₂₋₈ alkylene radical; 15 R₆ is selected from the group consisting of C₁₋₂₀ alkyl, C₆₋₉ cycloalkyl and phenyl; n, x, and z are numbers from 1 to 100; y is 0 to 100; m is 2 to 1000; 20 the ratio of x to (y+z) is from 1:10 to 10:1 and the ratio of y:z is from 5:1 to 1:100; i) a copolymer of oxyalkyleneglycol-alkenyl ethers and unsaturated dicarboxylic acids, comprising: 0 to 90 mol % of at least one component of the formula 3a or i) 25 3b:

wherein M is a hydrogen atom, a mono- or divalent metal cation, an ammonium ion or an organic amine residue, a is 1, or when M is a divalent metal cation a is ½;

wherein X is -OMa,

-O-(C_mH_{2m}O)_n-R¹ in which R¹ is a hydrogen atom, an aliphatic hydrocarbon radical containing from 1 to 20 carbon atoms, a cycloaliphatic hydrocarbon radical containing 5 to 8 carbon atoms or an optionally hydroxyl, carboxyl, C₁₋₁₄ alkyl, or sulphonic substituted aryl radical containing 6 to 14 carbon atoms, m is 2 to 4, and n is 0 to 100,

-NHR₂,-N(R^2)₂ or mixtures thereof in which R^2 = R^1 or -CO-NH₂; and

wherein Y is an oxygen atom or -NR²;

ii) 1 to 89 mol% of components of the general formula 4:

$$---CH_2$$
 $---CR^3$ (4)
 $(CH_2)_p$ $----O$ $(C_mH_{2m}O)_n$ $----R^1$

wherein R₃ is a hydrogen atom or an aliphatic hydrocarbon radical containing from 1 to 5 carbon atoms, p is 0 to 3, and R₁ is hydrogen, an aliphatic hydrocarbon radical containing from 1 to 20 carbon atoms, a cycloaliphatic hydrocarbon radical containing 5 to 8 carbon atoms or an optionally hydroxyl, carboxyl, C₁₋₁₄ alkyl, or sulfonic substituted

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aryl radical containing 6 to 14 carbon atoms, m is 2 to 4, and n is 0 to 100, and

iii) 0.1 to 10 mol % of at least one component of the formula 5a or 5b:

$$\begin{array}{c|c}
 & R^4 \\
\hline
 & C \\
 & C \\
\hline
 & S & T
\end{array}$$
(5a)

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wherein S is a hydrogen atom or $-COOM_a$ or $-COOR_5$, T is $-COOR_5$, $-W-R_7$, $-CO-[-NH-(CH2)3)-]_s-W-R_7$, $-CO-(CH_2)_z-W-R_7$, a radical of the general formula:

$$---U^{1} \left(CH - CH_{2} - O \right)_{x} \left(CH_{2} - CH_{2} - O \right)_{y} R^{6}$$

$$CH_{3}$$

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or $-(CH_2)_z$ -V- $(CH_2)_z$ -CH=CH-R₁, or when S is $-COOR_5$ or $-COOM_a$, U₁ is -CO-NHM-, -O- or $-CH_2O$, U₂ is -NH-CO-, -O- or $-OCH_2$, V is -O-CO-C₆H₄-CO-O- or -W-, and W is

$$\begin{array}{c|c} CH_3 & CH_3 \\ \hline Si & O & Si \\ \hline CH_3 & CH_3 \\ \hline CH_3 & CH_3 \\ \end{array}$$

R4 is a hydrogen atom or a methyl radical, R5 is an aliphatic hydrocarbon radical containing 3 to 20 carbon atoms, a cycloaliphatic hydrocarbon radical containing 5 to 8 carbon atoms or an aryl radical containing 6 to 14 carbon atoms, $R_6 = R_1$ or

$$-$$
CH₂ $-$ CH $-$ U² $-$ C=CH $-$ H $-$ R⁴ $-$ R⁴ $-$ S

 $R_7 = R_1$ or

$$--\left\{ \left(CH_{2}\right) _{3}--NH\right\} _{S}CO--C=CH$$

or

r is 2 to 100, s is 1 or 2, x is 1 to 150, y is 0 to 15 and z is 0 to 4;

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iv) 0 to 90 mol % of at least one component of the formula 6a, 6b, or 6c:

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wherein M is a hydrogen atom, a mono- or divalent metal cation, an ammonium ion or an organic amine residue, a is 1, or when M is a divalent metal cation a is $\frac{1}{2}$;

wherein X is -OM_a,

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-O-(C_mH_{2m}O)_n-R¹ in which R¹ is a hydrogen atom, an aliphatic hydrocarbon radical containing from 1 to 20 carbon atoms, a cycloaliphatic hydrocarbon radical containing 5 to 8 carbon atoms or an optionally hydroxyl, carboxyl, C₁₋₁₄ alkyl, or sulphonic substituted aryl radical containing 6 to 14 carbon atoms, m is 2 to 4, and n is 0 to 100,

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 $-NH-(C_mH_{2m}O)_n-R^1$,

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-NHR₂,-N(R^2)₂ or mixtures thereof in which R^2 = R^1 or -CO-NH₂; and

wherein Y is an oxygen atom or -NR²;

- j) a copolymer of dicarboxylic acid derivatives and oxyalkylene glycolalkenyl ethers, comprising:
 - i) 1 to 90 mol. % of at least one member selected from the group consisting of structural units of formula 7a and formula 7b:

$$\begin{array}{c|c} \hline CH \hline CH \hline \\ \hline \\ COOM_a \\ \hline \end{array} COR^1$$
 (7a)

$$\begin{array}{c|c}
CH & CH \\
\hline
C & O
\end{array}$$
(7b)

wherein M is H, a monovalent metal cation, a divalent metal cation, an ammonium ion or an organic amine;

a is ½ when M is a divalent metal cation or 1 when M is a monovalent metal cation;

wherein R1 is -OMa, or

 $-O-(C_mH_{2m}O)_n-R^2$ wherein R^2 is H, a C_{1-20} aliphatic hydrocarbon, a C_{5-8} cycloaliphatic hydrocarbon, or a C_{6-14} aryl that is optionally substituted with at least one member selected from the group consisting of $-COOM_a$, $-(SO_3)M_a$, and $-(PO_3)M_{a2}$;

m is 2 to 4; n is 1 to 200;

ii) 0.5 to 80 mol. % of the structural units of formula 8:

$$-CH_2 - CR^3 - (8)$$

$$(CH_2)_p - CR^3 - (C_mH_{2m}O)_n - R^2$$
is H or a Conslination hydrogeneous

wherein R³ is H or a C1-5 aliphatic hydrocarbon;

p is 0 to 3;

 R^2 is H, a C_{1-20} aliphatic hydrocarbon, a C_{5-8} cycloaliphatic hydrocarbon, or a C_{6-14} aryl that is optionally substituted with at least one member selected from the group consisting of $-COOM_a$, $-(SO_3)M_a$, and $-(PO_3)$ M_{a2} ;

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m is 2 to 4; n is 1 to 200;

iii) 0.5 to 80 mol.% structural units selected from the group consisting of formula 9a and formula 9b:

wherein R^4 is H, C_{1-20} aliphatic hydrocarbon that is optionally substituted with at least one hydroxyl group, $-(C_mH_{2m}O)_{n-}R^2$, — CO-NH- R^2 , C_{5-8} cycloaliphatic hydrocarbon, or a C_{6-14} aryl that is optionally substituted with at least one member selected from the group

M is H, a monovalent metal cation, a divalent metal cation, an ammonium ion or an organic amine;

a is ½ when M is a divalent metal cation or 1 when M is a monovalent metal cation;

 R^2 is H, a C_{1-20} aliphatic hydrocarbon, a C_{5-8} cycloaliphatic hydrocarbon, or a C_{6-14} aryl that is optionally substituted with at least one member selected from the group consisting of $-COOM_a$, $-(SO_3)M_a$, and $-(PO_3)M_{a2}$;

m is 2 to 4; n is 1 to 200;

iv) 1 to 90 mol. % of structural units of formula 10

consisting of $-COOM_a$, $-(SO_3)M_a$, and $-(PO_3)M_{a2}$;

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$$\begin{array}{c|c}
R^6 \\
\hline
\\
CH - C - \\
R^5 R^7
\end{array} (10)$$

wherein R⁵ is methyl, or methylene group, wherein R⁵ forms one or more 5 to 8 membered rings with R⁷;

R⁶ is H, methyl, or ethyl;

R⁷ is H, a C₁₋₂₀ aliphatic hydrocarbon, a C₆₋₁₄ aryl that is optionally substituted with at least one member selected from the group consisting of -COOM_a, -(SO₃)M_a, and -(PO₃)M_a², a C₅₋₈ cycloaliphatic hydrocarbon, -OCOR⁴, -OR⁴, and -COOR⁴, wherein R⁴ is H, a C₁₋₂₀ aliphatic hydrocarbon that is optionally substituted with at least one -OH, -(C_mH_{2m}O)_n-R², -CO-NH-R², C₅₋₈ cycloaliphatic hydrocarbon, or a C₆₋₁₄ aryl residue that is optionally substituted with a member selected from the group consisting of -COOM_a, -(SO₃)M_a, and -(PO₃)M_{a2}.

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